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Abstract

The resonance frequency of AFM cantilevers depends on the elastic modulus and on the dimensions of the cantilever. As for coated cantilevers, the resonance frequency will be determined not only by the properties of the cantilever, but also by the properties of the coating (elastic modulus and thickness). We have carried out a systematic investigation of cantilevers coated with several thicknesses of the DLC films. Measurements of the resonance frequency of the cantilevers, before and after the DLC coating, were used with a model to determine the elastic modulus of the DLC. The elastic modulus obtained for the DLC, with this model, was E_2 = 616 GPa. The AFM tip radii were also measured after coating and were found to increase with the DLC film thickness.

1. Introduction

Diamond-like carbon (DLC), also called amorphous diamond or amorphous carbon or tetrahedrally bonded amorphous carbon, is a new kind of superhard material containing both graphitically bonded carbon (sp^2) and diamond-bonded carbon (sp^3). The higher the sp^3:sp^2 ratio, the more diamond-like the material performs, quite generally for all its properties. DLC has been made using a variety of techniques. The material may be hydrogenated, however the highest sp^3:sp^2 materials are hydrogen-free. A necessary ingredient to the DLC thin film formation process is that the carbon ions be deposited somewhat energetically, with an ion deposition energy in the broad range from a few tens of electron volts up to a few hundred electron volts, with the optimum (maximum sp^3:sp^2) energy being about 100 – 150 eV [1 - 4]. Thus low energy film deposition techniques such as evaporation do not result in the formation of true DLC. Plasma-based methods in which the carbon ion deposition energy can be controlled and adjusted in the vicinity of 100 eV are appropriate, and can be based on the use of plasmas formed from hydrocarbon precursor gases such as methane, or on pure carbon plasmas. Properties of DLC and methods for forming this important new thin film material have been widely discussed in the literature [5].

The Atomic Force Microscopy (AFM) is a very powerful tool to characterize surfaces. Several modes of operation have been developed with this technique: the contact mode, during which the tip remains in contact with the surface, and the noncontact mode. In addition, several methods involve oscillating the cantilever. The AFM cantilevers are manufactured using photolithography and are commercially available in a wide range of materials, dimensions and force constants. The most commonly used materials are single crystalline Si and Si_3N_4. One of the challenges with this technique is how the tip affects or is affected by the measurements. Of relevance to this paper is the fact that when analyzing hard materials, standard tips are worn out as they are scanned across the surface. In such cases, tips made out of or coated with hard materials are highly desirable. In this paper, we have examined the effect of DLC coating on the resonance frequency as well as tip radius of the AFM cantilever.

The AFM has been shown to be a very sensitive tool to record changes in the cantilever resonance frequency [6, 7], since this equipment has the capability to measure resonance frequencies of the cantilevers, as part of the oscillation mode procedure. We have carried out a systematic investigation of cantilevers coated with several thicknesses of the DLC films. The resonance frequency of AFM cantilevers depends on the elastic modulus and on the dimensions of the cantilever. As for coated cantilevers, the resonance frequency will be determined not only by the properties of the cantilever, but also by the properties of the coating (elastic modulus and thickness). Measurements of the resonance frequency of the cantilevers, before and after the DLC coating, were used with a model [8] to determine the elastic modulus of the DLC. Furthermore, the tip radii were measured after coatings and were found to increase with DLC film thickness.

2. Materials and Methods

DLC deposition

Thin films of a wide range of materials can be fabricated using the dense metal plasma formed by a vacuum arc discharge embodied as in a “metal plasma immersion ion implantation and deposition (MePIIID)” configuration [2 – 4, 9, 10]. This technique is highly effective for producing high quality DLC films, and has been described in detail elsewhere [5, 11 - 14]. In this approach, a carbon plasma is formed from a vacuum arc plasma gun [15], and allowed to stream toward a substrate that can be repetitively pulse-biased to a chosen bias voltage. Hydrogen-free DLC films have been made that are ion stitched to the substrate and with hardness up to 60 GPa, adhesion >80 MPa, density 2.9 g/cm^3, and sp^3 (diamond bonding) fraction up to 85%.

In this work, the parameters used for the DLC deposition were: 150 A for the arc current, with 20 ms for arc duration and the frequency of the pulses was 1 Hz. It is known that DLC films produced by MePIIID are highly stressed, therefor a uniform coating around the cantilever is important to prevent bending. To have a uniform coating around the cantilever, we used a rotating holder, as it is illustrated in Figure 1. The rotation frequency of the holder was 2.5 rpm, which means that in each complete turn the plasma gun has been shot 24 times, covering the cantilever, and the tip probe, uniformly around the direction perpendicular to the rotation axis.

The thickness of the film was measured using a small piece of silicon, rotating together with the cantilever, with an ink mark. After the deposition, the ink was removed and the step was measured by profilometry. In one of the depositions we have also coated a silicon piece, for thickness control, but not attached to the rotating holder, so we could compare the rate deposition for a rotating sample and the conventional rate deposition for this technique.

AFM Method

The AFM cantilevers used in this work were made out of single crystalline silicon. Figure 2 presents the morphology of the cantilevers and the corresponding tips used. This kind of cantilever is typically used for AFM oscillation mode. The figure shows a silicon etched cantilever, with a trapezoidal cross-section, having the following nominal dimensions: the length (l) of the cantilever is 125 μm, the thickness (t) is between 3.5 and 5 μm and the width (w) is between 30 and 40 μm.

The measurements consist of first measuring the resonance frequency of the as-received cantilevers. These measurements have been done using a NanoScope IIIA microscope in AFM mode. This equipment has this capability as part of the oscillation mode procedure. Then, cantilevers were coated with DLC, as described above. Then the resonance frequency of each cantilever was measured again. The measured frequencies and the DLC thicknesses of the cantilevers were used to determine the DLC elastic modulus, using a mathematical model to be described below [8].

To measure the tip radius, we have applied the method using a $SrTiO_3$ single crystal. This crystal has the surface facets in the planes (101) and (103) making very sharp ridges. The tip radius is determined by scanning over these ridges. The images of the top of the ridges gives the tip profile, which can be determined by fitting the data with a polynomial of second order [16, 17].

Modeling to determine the elastic modulus

In this model [8] the resonance frequency for the uncoated cantilevers (ν_u) is given by:

$$\nu_u = \frac{1}{2\pi}\sqrt{\frac{k}{m^*}} = \frac{1.02}{2\pi l^2}\sqrt{\frac{E}{\rho}} \qquad \text{(I)}$$

where k is the force constant, m* is the effective mass, l is the length of the cantilever, E is the elastic modulus and ρ is the density. Here we have assumed that the cantilever has a rectangular cross section and m* = 0.24 m, m being the cantilever mass.

For a thin and uniform coating, with thickness δ, the resonance frequency for the coated cantilevers (ν_c) is given by:

$$\nu_c = \frac{3.52t}{2\pi l^2}\sqrt{\frac{E_1\frac{wt}{12} + E_2\delta\left(\frac{w}{2}+\frac{t}{6}\right)}{\rho_1 tw + 2\rho_2\delta(w+t)}} \qquad \text{(II)}$$

where l , t and w are the length, thickness and width of the uncoated cantilever, E_1 and ρ_1 are the elastic modulus and density of the silicon cantilever, E_2 and ρ_2 the elastic modulus and density of the coating [8]. The values of 102 GPa and 2.3 g/cm^3 are used for the elastic modulus and density of silicon, respectively. The density of DLC, ρ_2, is 2.9 g/cm^3 [1]. In order to normalize the resonance frequency, the ratio ν_c/ν_u is plotted as a function of the film thickness.

The elastic modulus E_2 of the DLC is then calculated by fitting the theoretical frequency ratio, ν_c/ν_u, determined from equation I and II, to the experimentally measured frequency ratio, according to the model described in reference [8].

3. Results and Discussions

We have compared the deposition rates on the stationary substrate and the rotating one and have obtained a factor of 3.2 between the two deposition rates. The relative depositions that can be expected on stationary vs. rotating substrates can be considered in the following way. The rotating substrate can be though of as a small section of a "virtual cylinder" that rotates. The deposition rate on the surface of the cylinder, in the absence of sputtering effects, is lower than on a flat substrate normal to the plasma flow (i.e., stationary substrate) by the ratio of the cylinder circumference to cylinder diameter – a factor of π. Thus the film thickness accumulated on a stationary substrate is expected to be greater than the film thickness accumulated on a rotating substrate by a factor of about 3.2, which is indeed precisely as observed. Note that this is a "zero-sputtering limit"; more energetic ion deposition would be expected to lead to higher sputtering, especially at glancing angles of incidence, and the deposition ratio factor would increase to around 5 to 6 depend on the details of the sputtering.

The measured frequencies of the cantilevers, before and after the DLC deposition, are presented in Table 1, with the respective thicknesses of the DLC films deposited. Note that, the thicknesses of the films were obtained with a Si sample attached with the cantilever in the rotating holder, as described above. The frequency increases with DLC thickness, indicating an increase in stiffness.

The elastic modulus E_2 of the DLC was determined, fitting the theoretical frequency ratio, ν_c/ν_u (equation (I) and (II)), to the measured frequency ratio, in function of the film thickness. In Figure 3, the circles correspond to the experimental data and the curve corresponds to the theoretical fitting. The elastic modulus obtained with this fitting was E_2 = 616 GPa. This value is higher than those determined by nanoindentation techniques [1], but compares well with a recent determination of elastic modulus by Brilluoin scattering (580 GPa) [14]. The values determined by nanoindentation tend to underestimate the actual modulus, because they are more strongly affected by the substrate.

Most of the tip radii, measured using a $SrTiO_3$ single crystal, are presented in Table II. Note that in this table we have introduced an original tip, presenting the nominal tip radius of 50 nm. Tips B and C were damaged, during the manipulation and several measurements, so their radii are not presented.

Although we assume a nominal tip radius of 50 nm, it is known that some variation of radius can be expected from tip to tip. This may explain in part the apparent discrepancy of the radii of tips A and D: the tip radius is smaller for thicker DLC film. In spite of that, we observed a direct correlation between the tip radius and the DLC thickness, as shown in Figure 4. The experimental data plotted in Figure 4 was fitted to a straight line, using the least square method, resulting in a calculated slope of 2.3.

4. Conclusions

In this work we have used a successful method to coat AFM cantilevers with DLC thin films. The resonance frequency of the cantilever increased with the film thickness, as it was expected by using a theoretical model. The elastic modulus obtained for the DLC, with this model, was E_2 = 616 GPa. We also observed that the radius of the AFM tips increased with the DLC thickness.

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References

[1] G.M. Pharr, D.L. Callahan, S.D. McAdams, T.Y. Tsui, S. Anders, A. Anders, J.W. Ager III, I.G. Brown, C.S. Bhatia, S.R.P. Silva, J. Robertson, Appl. Phys. Lett. **68** (6), 779 (1996).

[2] A. Anders, Surf. Coat. Technol., **93**, 158-167 (1997).

[3] I.G. Brown, *Annual Review of Materials Science*, Vol. 28, (Annual Reviews, Inc., Palo Alto, CA, 1998).

[4] O.R. Monteiro, Nucl. Instrum. Meth. Phys. Res. **B148**, 12-16 (1999).

[5] See, for instance, Proceedings of the 10th European Conference on Diamond, Diamond-like Materials, Carbon Nanotubes, Nitrides and Silicon Carbide, in Diamond Relat. Mater. **9**, 231-1306 (2000) [Vol. 9, Nos.3-6, April/May, 2000].

[6] T. Thundat, G.Y. Chen, R.J. Warmack, D.P. Allison, E.A. Wachter, Anal. Chem. **67** (3), 519 (1995).

[7] J.P. Cleveland, S. Manne, D. Bocek, P.K. Hansma, Rev. Sci. Instrum. **64** (2), 403 (1993).

[8] C. Stoldt, M.C. Fritz, C. Carraro and R.Maboudian, manuscript in preparation (2001).

[9] J.V. Mantese, I.G. Brown, N.W. Cheung and G.A. Collins, Plasma Processing of Advanced Materials, MRS Bulletin **21**(8), 52-56 (1996).

[10] I.G. Brown, A. Anders, M.R. Dickinson, R.A. MacGill and O.R. Monteiro, Surf. Coat. Technol. **112**, 271-277 (1999).

[11] S. Anders, A. Anders, J.W. Ager III, Z. Wang, G.M. Pharr, T.Y. Tsui, I.G. Brown and C.S. Bhatia, Mat. Res. Soc. Symp. Proc. **383**, 453 (1995).

[12] G.M. Pharr, D.L. Callahan, S,D. McAdams, T.Y. Tsui, S. Anders, A. Anders, J.W. Ager I.G. Brown, C.S. Bhatia, S.R.P. Silva and J. Robertson, Appl. Phys. Lett. **68**, 779-781 (1996).

[13] O.R. Monteiro, M.-P. Delplancke-Ogletree, J.W. Ager and I.G. Brown, Mat. Res. Soc. Symp. Proc. **438**, 599-604 (1997).

[14] O.R. Monteiro, I.G. Brown, R. Sooryakumar and M. Chirita, Mat. Res. Soc. Symp. Proc. **444**, 93-98 (1997).

[15] R.A. MacGill, M.R. Dickinson, A. Anders, O.R. Monteiro and I.G. Brown, Rev. Sci. Instrum. **69**, 801-803 (1998).

[16] D.F. Ogletree, R.W. Carpick, M. Salmeron, Review of Scientific Instruments **67** (9), 3298 (1996).

[17] M.C. Fritz, PhD Dissertation, Swiss Federal Institute of Technology, Zurich, Switzerland, 2000.

Table Captions

Table 1: Measured frequencies of the cantilevers, before and after the DLC deposition, and the respective thicknesses of the DLC films deposited.

Table 2: Measured tip radii and the respective thicknesses of the DLC films deposited. This table includes the nominal radius of an original tip. The tips B and C were damaged, during the manipulation and several measurements, so their radii are not presented.

Figure Captions

Figure 1: Scheme for rotating the sample holder used for the DLC deposition.

Figure 2: Scanning electron micrographs showing: (a) the typical morphology of the cantilevers used in this work and (b) an image of the tip in larger magnification.

Figure 3: Plot of the frequency ratio, ν_c/ν_u, as a function of the film thickness. The circles correspond to the experimental data and the curve corresponds to the theoretical fitting.

Figure 4: Plot of the tip radii as a function of the thicknesses of the DLC films.

Table I

Cantilever	Original Frequency ν_u (kHz)	Thickness of the DLC film (nm)	Frequency after the DLC deposition ν_c (kHz)
A	281.7	28	291.7
B	271.8	47	298.5
C	277.5	90	323.0
D	293.2	106	347.0
E	285.8	145	357.3
F	287.4	283	413.8

Table II

Tip	Thickness of the DLC film (nm)	Tips radii (nm)
Original	0	50
A	28	252
B	47	-
C	90	-
D	106	200
E	145	374
F	283	774